Anal. Calcd. for $C_{25}H_{29}O_7N$: C, 65.92; H, 6.42; N, 3.08. Found: C, 66.09; H, 6.23; N, 3.21.

The infrared spectrum (Nujol) showed peaks at 5.65, 5.77, and 5.99 μ, and no NH or OH absorption.

Upon treatment with warm methanol, this compound released acetic acid (Calcd. $C_2H_4O_2$, 13.2%. Found: 12.8%) and formed the compound in which *the aliphatic acetoxyl group is replaced by methoxyl*. Recrystallization of this product from cyclohexane–ethyl acetate afforded colorless, cottony crystals, m.p. 129–131°. The infrared spectrum (Nujol) showed that the phenolic acetate and *N*-acetyl groups (5.69 and 6.02 μ, respectively) were retained, while the original acetoxy (5.77 μ) peak was absent.

Anal. Calcd. for $C_{24}H_{29}O_6N$: C, 67.43; H, 6.84; N, 3.28; OCH_3, 21.8. Found: C, 67.57; H, 6.63; N, 3.35; OCH_3, 20.4.

Both this compound and its triacetate precursor were hydrolyzed by boiling with 5% sodium hydroxide solution for a few minutes to give *1-acetylamino-5,6,7,8-tetrahydro-2-naphthol;* m.p. 196–198°, after recrystallization from ethyl acetate. The compound gave a green ferric chloride test.

Anal. Calcd. for $C_{12}H_{15}O_2N$: C, 70.21; H, 7.37; N, 6.83. Found: C, 70.33; H, 7.19; N, 6.90.

Compound VII. A solution of 20 g. of veratraldehyde and 8 g. of ethanolamine in 300 ml. of benzene was refluxed under a water-separator for 1 hr. Evaporation of the solvent, and trituration of the crystalline residue with benzene, gave 23.7 g. of colorless crystals, m.p. 102–104°. Recrystallization from ethyl acetate raised the m.p. to 104–105°.

Anal. Calcd. for $C_{11}H_{15}O_3N$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.25; H, 7.51; N, 6.62.

Reduction of this compound with sodium borohydride in methanol by the usual procedure afforded a quantitative yield of yellow, oily *hydroxyamine*, which was characterized by preparing the *O,N-diacetate* (VIII): the oil was refluxed with excess acetic anhydride for 2 hr., and after evaporation of the reagent, the product was recrystallized from cyclohexane–ethyl acetate; colorless crystals, m.p. 91–92°.

Anal. Calcd. for $C_{15}H_{21}O_5N$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.96; H, 7.12; N, 4.74.

When 5 g. of Compound VII and 50 ml. of acetic anhydride were refluxed for 1 hr., there was isolated 1.6 g. of veratraldehyde, after careful trituration of the crude product with ethyl acetate.

Acknowledgment. It is a pleasure to thank the following members or former members of Mr. Louis Dorfman's staff for microanalytical and spectrophotometric work: Mr. George Robertson, Miss Natalie Cahoon, Miss Patricia Gallant, Mrs. Violet Loire, Miss Margaret Jones, Mrs. Vivian Scarinza, and Mr. Herbert Behrens; and Mr. Dorfman himself for interesting discussion on various aspects of spectra involved in this work. Assistance with the preparation of some of the compounds was also rendered by Misses Patricia Wenk and Barbara Weaver.

SUMMIT, N. J.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF NORTH DAKOTA AND HOFSTRA COLLEGE]

Angular-Substituted Hydrocarbazoles. I. 6-Benzenesulfonamido-4-keto-9-benzenesulfonyl-11-methyl-2,3,4,11-tetrahydrocarbazole[1,2]

RICHARD R. HOLMES, KARL G. UNTCH, AND HARVEY D. BENSON

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Synthesis of an angular-substituted 4-ketotetrahydrocarbazole, 6-benzenesulfonamido-4-keto-9-benzenesulfonyl-11-methyl-2,3,4,11-tetrahydrocarbazole, by the addition of active methylene compounds to quinone diimides, is described. 1,3-Cyclohexanedione, 2-methyl-1,3-cyclohexanedione, and 2-carbethoxymethyl-1,3-cyclohexanedione were added to *p*-quinonedibenzenesulfonimide and the products cyclized to indoles. The cyclohexanedione ring in the adducts was cleaved by heating with acetic acid and indoles were formed. Dilute alkali also induced cleavage of the cyclohexanedione ring, with formation of indoles. Acetic anhydride in pyridine cyclized the adduct from 2-methyl-1,3-cyclohexanedione and *p*-quinonedibenzenesulfonimide to the *N*-acetyl derivative of 6-benzenesulfonamido-4-keto-9-benzenesulfonyl-11-methyl-2,3,4,11-tetrahydrocarbazole, without ring cleavage; but with 2-(2,5-dibenzenesulfonamidophenyl)-2-carbethoxymethylcyclohexane-1,3-dione acetic anhydride gave a carbostyril, which appears to be the preferred course when such a mode of cyclization is possible.

Although the total synthesis of strychnine has been accomplished,[3] a search for simpler routes to strychnine-like substances is still desirable. The present paper describes the synthesis of an angular-substituted hydrocarbazole of interest in connection with the synthesis of substances related to strychnine.

Adams and Blomstrom[4] found that *p*-quinonedibenzenesulfonimide would add active methylene compounds in the presence of catalytic amounts of sodium methoxide, and Adams and Samuels[5] developed an excellent indole synthesis based upon cyclization of these adducts. It occurred to the present authors that a similar series of reactions applied to a 2-substituted 1,3-cyclohexanedione might, if successful, constitute a useful route to angular-substituted 4-ketotetrahydrocarbazoles of the type I. Furthermore, if the angular group were

(1) Abstracted in part from the M.S. theses of Karl G. Untch, University of North Dakota, 1955, and Harvey D. Benson, University of North Dakota, 1956.

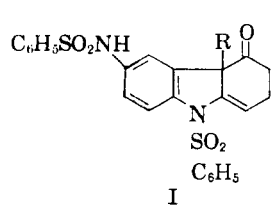
(2) The authors would like to thank the Research Corp. of New York for generous grants in support of this investigation.

(3) R. B. Woodward *et al.*, *J. Am. Chem. Soc.*, **76**, 4749 (1954).

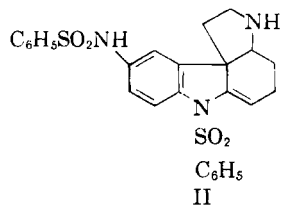
(4) R. Adams and D. C. Blomstrom, *J. Am. Chem. Soc.*, **75**, 3403 (1953).

(5) R. Adams and W. P. Samuels, *J. Am. Chem. Soc.*, **77**, 5375, 5383 (1955).

suitably chosen (R = —$CCNO_2$ or —CCN, for example) the possibility of reductive cyclization to a substance of the general structure II, containing four of the rings present in strychnine would make the method very interesting indeed. Choice of a more highly substituted cyclohexanedione as starting material might enable one to construct more of the strychnine ring system.

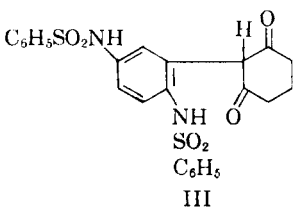


I

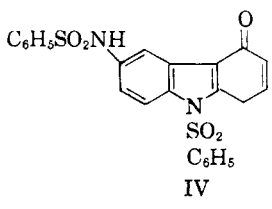


II

The present work started with an investigation of the Michael reaction between *p*-quinonedibenzenesulfonimide and 1,3-cyclohexanedione. A product melting at 173–178°, presumably adduct III, was obtained in excellent yield, but it was not analyzed, for attempts to recrystallize it gave a new substance, melting at 233–235° which, on the basis of elementary analysis, was formulated as tetrahydrocarbazole (IV). The substance was best prepared by boiling adduct III with glacial acetic acid when IV was produced in 98% yield. The extraordinary ease with which cyclization occurred was surprising, since Adams and Samuels[3] carried out their cyclizations of similar compounds under much more vigorous conditions (hot concentrated hydrochloric acid, or concentrated sulfuric acid at room temperature).



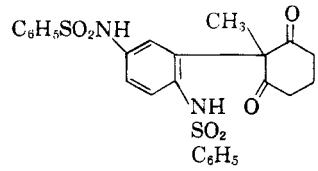
III



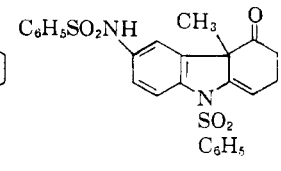
IV

Addition of 2-methyl-1,3-cyclohexanedione to *p*-quinonedibenzenesulfonimide also occurred in high (96%) yield. This result was particularly gratifying, since attempts by Stetter and Coenen[6] to add 2-substituted 1,3-cyclohexanediones to α,β-unsaturated esters and nitriles (using sodium ethoxide as catalyst, in ethanol) resulted in cleavage of the cyclohexanedione ring, and it was feared that a similar cleavage might be encountered in the addition of 2-methylcyclohexane-1,3-dione to *p*-quinonedibenzenesulfonimide.

Boiling glacial acetic acid did not convert adduct V into ketotetrahydrocarbazole (VI), but into a substance isomeric with the original adduct which was, however, soluble in dilute aqueous bicarbonate and was therefore a carboxylic acid. The ultraviolet absorption spectrum of this acid showed

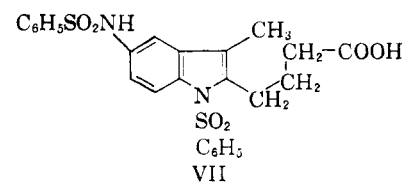


V



VI

(ethanol solution) an intense peak at 220 mμ; a shoulder at 233 mμ; a somewhat less intense peak at 263 mμ; and a relatively weak plateau in the general region of 315 mμ. Examination of the list of peaks in the ultraviolet absorption spectra of the 5-aminoindole derivatives prepared by Adams and Samuels[5] indicates that there are four regions of peak absorption more or less characteristic of this type of molecule; intense absorption at 210–240 mμ; a peak or inflection of somewhat lower intensity (not always discernible) at 230–240 mμ; a less intense peak at 260–280 mμ; and an inflection or plateau of relatively low intensity at about 300–320 mμ. All of these features were observed in the spectrum of the substance obtained by boiling V with acetic acid. Potentiometric titration gave a neutral equivalent of 547, in fair agreement with that expected (513) for a monobasic acid $C_{25}H_{24}N_2O_6S_2$. The titration curve showed two points of inflection; one corresponding to a strongly acidic group of apparent pK_a about 5.9, and the other to a weakly acidic group of apparent pK_a about 9.5. These values correspond to those expected for —COOH and —SO_2NH— groups. The same quantity of base was required to neutralize the weakly acidic as the strongly acidic group. The substance was therefore assigned structure VII.

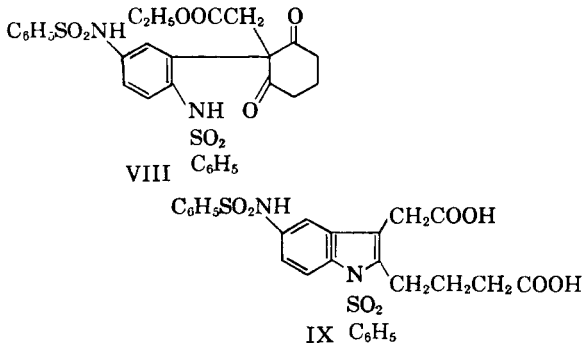


VII

Addition of 2-carbethoxymethyl-1,3-cyclohexanedione to *p*-quinonedibenzenesulfonimide also took place in high (89%) yield. When adduct VIII was boiled with glacial acetic acid a new substance was obtained, which, according to the analytical data, differed from VIII by loss of the elements of ethylene. The new substance was a carboxylic acid of neutral equivalent 278.4 (theory for $^1/_2$ of $C_{26}H_{24}N_2O_8S_2$: 278.3). To reach a second, less sharp, point of inflection in the titration curve addition of a further quantity of alkali equal to one-half that required to neutralize the strongly acidic groups, was required, so that the presence of two —COOH groups and one —SO_2NH— group was inferred. The ultraviolet absorption spectrum of the substance was almost identical with that of VII, indicating that it was also a 5-aminoindole derivative. The infrared spectrum (discussed in the experi-

(6) H. Stetter and M. Coenen, *Ber.*, **87**, 990 (1954).

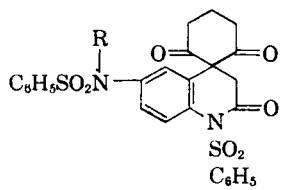
mental section) confirmed the presence of —SO_2-NH— and carboxyl groups. The substance was, therefore, IX.



VIII

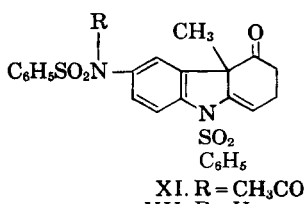
IX

The formation of IX from VIII by action of hot acetic acid is of special interest, for an alternative reaction path was conceivable, involving elimination of ethanol and formation of a lactam (X). But no lactam was found; in fact, the yield of IX was 98%.



X. R = H
XIII. R = CH_3CO

The reagent ultimately found to cyclize diketone V in the desired manner (without cleavage of the cyclohexanedione ring) was a mixture of acetic anhydride and pyridine. On boiling V with this reagent for a short time a new substance insoluble in aqueous sodium hydroxide was produced. Elementary analysis indicated that it differed from V by loss of the elements of water and gain of an acetyl group. Examination of the infrared spectrum (discussed in the experimental section) indicated the absence of —NH— or —OH groups and the presence of two kinds of carbonyl group, one absorbing in a region expected of an *N,N*-disubstituted amide, and the other in the region expected of a saturated, six-membered ring ketone. The substance was therefore assigned structure XI.



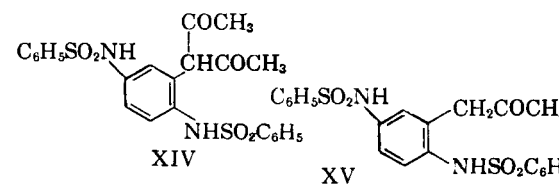
XI. R = CH_3CO
XII. R = H

Confirmation of this structure was obtained by hydrolysis of the acetyl group under mild conditions to give XII.

Treatment of keto-ester VIII with the acetic anhydride–pyridine reagent did not lead to an angular-substituted hydrocarbazole, but to *N*-acetyl-*N*-benzenesulfonyl-1-benzenesulfonyl-4-(1,-5-diketopentamethylene)-6-amino-3,4-dihydrocarbostyril (XIII).

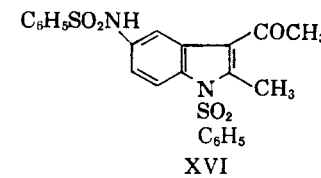
It is interesting to contrast the behavior of VIII on treatment with acetic acid and on treatment with the acetic anhydride–pyridine reagent. No doubt the difference is due to differences in relative rate of acid-catalyzed cyclization to hydrocarbazole *versus* amide formation in the two cases.

Other attempts to cyclize 2-(2,5-dibenzenesulfonamidophenyl)-2-methylcyclohexane-1,3-dione (V) without cleavage of the cyclohexanedione ring, including treatment with cold, concentrated sulfuric acid (a method which was successful in the hands of Adams and Samuels[5] when applied to a similar compound), with hot acetic anhydride, with heat alone, and with base, were unsuccessful. The extraordinary sensitivity to cleavage by base of the 1,3-diketone system in these adducts is well illustrated by the behavior of 3-(2,5-dibenzenesulfonamidophenyl)pentane-2,4-dione (XIV) (prepared by the method of Adams and Blomstrom[4]) on allowing a solution in 5% aqueous sodium hydroxide to stand at room temperature for an hour.



XIV XV

The only product isolated on acidification was 1-(2,5-dibenzenesulfonamidophenyl)propanone-2 (XV). The same cleavage was reported by Adams and Blomstrom[4] on prolonged boiling with sodium hydroxide solution, but it is surprising that cleavage occurred under the mild conditions used in the present work. Hot glacial acetic acid converted diketone XIV to 1-benzenesulfonyl-2-methyl-3-acetyl-5-benzenesulfonamidoindole (XVI) without



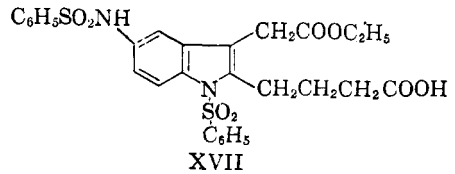
XVI

cleavage, in 95% yield. The value of the acetic acid method of cyclization is well illustrated in this case, for Adams and Samuels[5] were unable to cyclize XIV by treatment with hot concentrated hydrochloric acid (although the dimethanesulfonyl analog of XIV did cyclize to a 3-acetyl indole on similar treatment).

Cyclic diketone V was also cleaved rapidly at room temperature by dilute aqueous alkali, but, in contrast to the behavior of XIV just described, the product was not a ketone, but an indole (VII),

identical with that produced from V by the action of acetic acid.

When 2-(2,5-dibenzenesulfonamidophenyl)-2-carbethoxymethyl cyclohexane-1,3-dione (VIII) was treated with cold dilute base the product was 1-benzenesulfonyl-2-(3-carboxypropyl)-3-carbethoxymethyl-5-benzenesulfonamidoindole (XVII).



XVII

This result was interesting since it emphasized the fact that both cleavage and indole formation occurred readily under conditions so mild that the ester group was not attacked.

EXPERIMENTAL[7]

2-(2,5-Dibenzenesulfonamidophenyl)cyclohexane-1,3-dione (III). To a solution of 2.5 g. (0.015 mole) of *p*-quinonedibenzenesulfonimide[8] and 2.0 g. (0.018 mole) of cyclohexane-1,3-dione[9] in 260 ml. of purified[10] dioxane was added 30 mg. of dry sodium methoxide. After 20 min. at room temperature the bright yellow color of the solution had faded to a straw yellow. Acetic acid (1.2 ml.) was added; the solution was poured into 1100 ml. of water, and the white precipitate was removed and air-dried, when it (7.45 g., 99%) melted over the range 173–178°. Attempts to recrystallize the crude material from hot aqueous dioxane gave a new substance melting at 233–235°, shown to be identical (mixed melting point) with the substance IV described below.

1-Keto-5-benzenesulfonyl-3-benzenesulfonamido(1,2,3,4)-tetrahydrocarbazole (IV). A mixture of glacial acetic acid (180 ml.) and crude adduct III (5.7 g., 0.0114 mole, m.p. 173–178°) was refluxed for 1.5 hr.; water was added, and the solution was allowed to cool slowly. The product (5.4 g., 0.0112 mole, 98%) melted at 233–237°. The analytical sample, prepared by three recrystallizations from dioxane water, also melted at 235–237°.

Anal. Calcd. for $C_{24}H_{20}N_2O_5S_2$: C, 59.98; H, 4.10; N, 5.83. Found: C, 60.13; H, 3.88; N, 5.66.

2-(2,5-Dibenzenesulfonamidophenyl)-2-methylcyclohexane-1,3-dione (V). Sodium methoxide (0.8 g.) was added to a solution of *p*-quinonedibenzenesulfonimide (21.2 g., 0.55 mole) and 2-methylcyclohexane-1,3-dione[11] (6.2 g., 0.050 mole) in purified[10] dioxane (1100 ml.). After 15 min. at room temperature the mixture was added to 4200 ml. of distilled water, and the white precipitate was crystallized from hot ethanol water. The crude adduct V weighed 24.1 g. (0.047 mole, 94%) and melted at 162–165°. The analytical sample was obtained by dissolving the substance in the minimum of boiling ethanol, adding water until crystals appeared, and then cooling (process repeated four times), and melted at 164–166°.

Anal. Calcd. for $C_{25}H_{24}N_2O_6S_2$: C, 58.57; H, 4.72; N, 5.47. Found: C, 58.81; H, 4.99; N, 5.30.

1-Benzenesulfonyl-2-(3-carboxypropyl)-3-methyl-5-benzenesulfonamidoindole (VII). A mixture of glacial acetic acid (35 ml.) and adduct V (1.0 g., 0.00195 mole) was refluxed for 2.5 hr., then poured into 200 ml. water. The gummy solid was dissolved in the minimum of boiling ethanol; water was added until crystals appeared; and the solution was allowed to cool. The colorless crystals (0.80 g., 0.00156 mole, 80%) melted at 206–209°.

Anal. Calcd. for $C_{25}H_{24}N_2O_6S_2$: C, 58.57; H, 4.72; N, 5.47. Found: C, 58.34; H, 4.85; N, 5.33.

The same material was obtained when 0.1 g. of adduct V was dissolved in 10% aqueous sodium hydroxide, the solution allowed to stand at room temperature for 5 min., and then acidified with cold 5% hydrochloric acid. The solid, after crystallization from the minimum of hot 1:1 ethanol-water, melted at 195–200°. A mixture with the sample (m.p. 206–209°) of VII obtained by heating adduct V with acetic acid melted at 197–204°.

The substance was soluble in 5% aqueous bicarbonate. A sample (0.0619 g., 1.21×10^{-4} mole) dissolved in 50 ml. of 1:1 by volume mixture of ethanol and water was titrated with standard sodium hydroxide using a *p*H meter to follow the course of the neutralization. Two breaks in the plot of ml. of base *vs.* *p*H were observed: One (apparent pK_a of 5.9) led to a neutral equivalent of 547 (theory for monobasic acid $C_{25}H_{24}N_2O_6S_2$: 512), and the other (apparent pK_a of 9.9) to a neutral equivalent of approximately 280 (theory for dibasic acid $C_{25}H_{24}N_2O_6S_2$: 256).

A solution of the substance VII in 95% ethanol (0.02 g., 3.9×10^{-5} mole, per l.) showed the following spectral features (Cary recording spectrophotometer); λ_{max} about 219 mμ, ϵ_{max} 40,700; shoulder about 233 mμ, ϵ_{max} 33,000; λ_{min} at 246 mμ, ϵ_{min} 23,000; λ_{max} at 263 mμ, ϵ_{max} 26,300; barely discernible shoulder at 274 mμ, ϵ_{max} 21,400; broad shoulder at about 312 mμ, ϵ_{max} about 2,000. The peak at 263 mμ is double with maxima at 261 and 266.

2-(2,5-Dibenzenesulfonamidophenyl)-2-carbethoxymethylcyclohexane-1,3-dione (VIII). Sodium methoxide (0.8 g.) was added to a solution of 26.0 g. (0.067 mole) of *p*-quinonedibenzenesulfonimide and 12.3 g. (0.062 mole) of 2-carbethoxymethylcyclohexane-1,3-dione[11] in purified dioxane (1300 ml.). After 10 min. at room temperature glacial acetic acid (4 ml.) was added and the solution was poured into 5 l. of water. The white solid was crystallized from the minimum of hot 95% ethanol and then weighed 32.2 g. (0.0552 mole, 89%). Four recrystallizations gave the analytical sample melting at 102° with decomposition.

Anal. Calcd. for $C_{28}H_{28}N_2O_9S_2$: C, 57.52; H, 4.82; N, 4.79. Found: C, 57.22; H, 5.24; N, 4.57.

1-Benzenesulfonyl-2-(3-carboxypropyl)-3-carboxymethyl-5-benzenesulfonamidoindole (IX). A mixture of adduct VIII (2.0 g., 0.00342 mole) and glacial acetic acid (50 ml.) was refluxed for 3 hr. Water was added, and the solution was allowed to cool undisturbed. The resulting colorless crystals (1.86 g., 0.00334 mole, 98%) melted at 218–219°.

Anal. Calcd. for $C_{26}H_{24}N_2O_8S_2$: C, 56.10; H, 4.35; N, 5.03. Found: C, 56.18; H, 4.17; N, 5.13.

A sample of 0.4269 g. (0.0007668 mole) of the substance in a mixture of 100 ml. water and 125 ml. ethanol was titrated with standard sodium hydroxide using a *p*H meter to follow the course of the neutralization. The graph of *p*H *vs.* quantity of base showed two breaks. The first (apparent pK_a about 5.8) led to a neutral equivalent of 278.4 (theory for dibasic acid $C_{26}H_{24}N_2O_8S_2$: 278.3). The second ill-defined break (apparent pK_a about 9.9) was reached on addition of very close to half again as much base as had been required to reach the first break in the titration curve and led to a neutral equivalent of 193 (theory for tribasic acid $C_{26}H_{24}N_2O_8S_2$: 185.5).

The infrared spectrum (potassium bromide pellet) of the substance contained a strong peak at about 1685 cm.$^{-1}$

(7) Microanalyses were performed by Clark Microanalytical Laboratories, Urbana, Ill. All melting points were obtained on a Kofler hot-stage, and are to be considered as corrected.

(8) R. Adams and A. S. Nagarkatti, *J. Am. Chem. Soc.*, 72, 4601 (1950).

(9) R. B. Thompson, *Org. Syn.*, 27, 21 (1947).

(10) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Co., 1941, p. 369.

(11) H. Stetter and W. Dierichs, *Ber.*, 85, 66 (1952).

(carboxyl —CO—, hydrogen-bonded[12]), and a peak at 3330–3390 cm.$^{-1}$ (carboxyl —OH, nonhydrogen-bonded[12]), with a broad shoulder centered at about 2650 cm.$^{-1}$ (carboxyl —OH, hydrogen-bonded[12]). A solution of the substance in 95% ethanol (0.02 g., 3.42 × 10^{-5} mole/l.) gave an ultraviolet spectrum almost identical with that of V: λ_{max} about 219 mμ, ϵ_{max} 41,600; shoulder 232 mμ, ϵ_{max} 32,400; λ_{min} 246 mμ, ϵ_{min} 21,800; λ_{max} 262 mμ, ϵ_{max} 25,000; shoulder at 273 mμ, ϵ_{max} about 20,000; broad shoulder about 312 mμ, ϵ_{max} about 2000. The peak at 263 mμ was double, with maxima at 261 and 266 mμ.

Action of alkali on 3-(2,5-dibenzenesulfonamidophenyl)-pentane-2,4-dione (XIV). When a solution of 3-(2,5-dibenzenesulfonamidophenyl)pentane-2,4-dione (0.5 g., 0.00103 mole) in 10 ml. of 10% aqueous sodium hydroxide was allowed to stand at room temperature for 1 hr., the solution acidified with dilute hydrochloric acid in the cold, and the solid recrystallized from hot ethanol water, the product (0.35 g., 0.00079 mole, 76%) was 1-(2,5-dibenzenesulfonamidophenyl)propanone-2 (XV) melting at 163–164°. Adams and Blomstrom[4] report a melting point of 165–166° for the compound. A mixture with the indole (XVI), m.p. 171–172° (see below) melted over the range 139–150°.

1-Benzenesulfonyl-2-methyl-3-acetyl-5-benzenesulfonamidoindole (XVI). A mixture of glacial acetic acid (40 ml.) and 3-(2,5-dibenzenesulfonamidophenyl)pentane-2,4-dione (2.5 g., 0.00514 mole) was refluxed for 24 hr. The solution was poured into water, and the white solid was recrystallized from the minimum of boiling 95% ethanol, when 2.2 g. (0.00460 mole, 89.5%) of XVI, melting sharply at 171–172°, was obtained.

Anal. Calcd. for $C_{23}H_{20}N_2O_5S_2$: C, 58.96; H, 4.30; N, 5.98. Found: C, 59.05; H, 4.49; N, 5.94.

A solution of the substance in 95% ethanol (0.02 g., 4.27 × 10^{-5} mole/l.) gave rise to the following ultraviolet absorption spectrum: λ_{max} 221 mμ, ϵ_{max} 51,300; shoulder at about 237 mμ, ϵ_{max} 30,200; shoulder at 260 mμ, ϵ_{max} 18,200; λ_{max} 266 mμ, ϵ_{max} 17,000; λ_{max} at 274 mμ, ϵ_{max} 15,800; very broad, bell-shaped shoulder from about 285–330 mμ, which overlapped the absorption at 266 and 274 mμ. Allowing for the overlap, the presence of a broad band with λ_{max} at about 290 mμ, ϵ_{max} about 12,300, was inferred. This feature was not present in the spectra of solutions of the related indoles VII and IX, and may therefore be attributed to the presence of the keto group in the 3-position of the indole ring. This band is presumably the analog, shifted to longer wave length by conjugation, of the usual[13] absorption of the isolated carbonyl group at about 270 mμ. The intensity is not far from that found for many α,β-unsaturated ketones —*e.g.*, *cis*-benzalacetophenone with λ_{max} 289 mμ, ϵ_{max} 8900.[14] No broad shoulder at about 312 mμ could be detected due to overlapping by this strong conjugated ketone band. Otherwise, the similarity to the absorption spectra of indoles VII and IX was rather striking. The enhanced intensity of the characteristic indole band at 221 mμ, as well as the small shift to longer wave lengths, can be explained readily in terms of the increased conjugation present in XVI. Woodward[15] has shown that the somewhat similar β-diketone enol-ether system absorbs strongly at 268 mμ with ϵ_{max} about 12,600—*i.e.*, with an intensity comparable to that observed for the band at about 290 mμ in the spectrum of XVI.

1-Benzenesulfonyl-2-(3-carboxypropyl)-3-carbethoxymethyl-5-benzenesulfonamidoindole (XVII). A solution of 0.50 g. (0.000856 mole) of 2-(2,5-dibenzenesulfonamidophenyl)-2-carbethoxymethylcyclohexane-1,3-dione (VIII) in 10% aqueous sodium hydroxide (15 ml.) was allowed to stand at room temperature for an hour, then acidified with cold 5% aqueous hydrochloric acid. An oil separated, which, after 2 weeks in contact with the mother liquors, crystallized. The crystals (0.32 g., 0.0060 mole, 70%) melted at 224–228°. Two recrystallizations from absolute ethanol gave a sample melting at 232–234°.

Anal. Calcd. for $C_{28}H_{28}N_2O_8S_2$: C, 57.52; H, 4.83; N, 4.79. Found: C, 57.99; H, 4.14; N, 4.76.

The substance gave a solution in aqueous ethanol which was acidic to litmus, and dissolved in cold 5% aqueous bicarbonate with evolution of carbon dioxide. Structure XVII was the only reasonable one for an acid of the above composition.

N-Acetyl,N-benzenesulfonyl-4-keto-6-amino-9-benzenesulfonyl-11-methyl(2,3,4,11)tetrahydrocarbazole (XI). To a solution of 8.5 g. (0.0166 mole) of 2-(2,5-dibenzenesulfonamidophenyl)-2-methylcyclohexane-1,3-dione (V) in pyridine (100 ml.) was added acetic anhydride (10 ml.) and the mixture was refluxed for 30 min. The cooled mixture was poured over crushed ice and allowed to stand overnight. The brown oil was dissolved in the minimum of hot 95% ethanol and the solution allowed to cool undisturbed, when a solid (7.5 g., 0.0142 mole, 85.5%) melting at 175–182° was obtained. After five recrystallizations from the minimum of hot 95% ethanol a sample melted at 186–187°.

Anal. Calcd. for $C_{27}H_{24}N_2O_6S_2$: C, 60.43; H, 4.51; N, 5.22. Found: C, 60.29; H, 4.01; N, 4.89.

The substance was insoluble in aqueous sodium hydroxide. Its infrared spectrum had no band in the 3100–3600 cm.$^{-1}$ (—OH and —NH stretching[12]) region, but strong bands at 1710 (ketonic —CO—[12]) and 1685 cm.$^{-1}$ (amide carbonyl[12]) and at 1360 and 1170 cm.$^{-1}$ (sulfonyl group[12]).

6-Benzenesulfonamido-4-keto-9-benzenesulfonyl-11-methyl-(2,3,4,11)tetrahydrocarbazole (XII). A solution of 4.0 g. (0.00745 mole) of *N*-acetyl-*N*-benzenesulfonyl-4-keto-6-amino-9-benzenesulfonyl-11-methyl-(2,3,4,11)-tetrahydrocarbazole (XI) in 50 ml. of a 5% solution of potassium hydroxide in 75% ethanol–25% water was heated slowly to the boiling point. The solution was allowed to cool to room temperature and, after 30 min., water (25 ml.) was added. Acidification with 5% aqueous hydrochloric acid gave a tan solid (2.0 g., 0.00405 mole, 54.5%) melting at 193–202°. Recrystallization from the minimum of ethylene dichloride, then from hot ethanol water, gave white crystals melting at 204–206°.

Anal. Calcd. for $C_{25}H_{22}N_2O_5S_2$: C, 60.71; H, 4.48; N, 5.66. Found: C, 61.23; H, 4.16; N, 5.41.

The substance was soluble in 5% aqueous sodium hydroxide but not in 5% bicarbonate solution. The infrared spectrum contained a strong band at 3180 cm.$^{-1}$ (—NH— group[12]) and strong bands at 1700 cm.$^{-1}$ (ketonic carbonyl group[12]), and 1370 and 1160 cm.$^{-1}$ (—SO_2— group[12]). Disappearance of the (amide[12]) band at 1685 cm.$^{-1}$ and appearance of the —NH— band at 3180 cm.$^{-1}$ on going from XI to XII is in harmony with the structures proposed for each of these compounds.

N-Acetyl,N-benzenesulfonyl-1-benzenesulfonyl-4-(1,5-diketopentamethylene)-6-amino-3,4-dihydrocarbostyril (XIII). To a solution of 2.0 g. (0.00342 mole) of 2-(2,5-dibenzenesulfonamidophenyl)-2-carbethoxymethylcyclohexane-1,3-dione (VIII) in 25 ml. of pyridine was added 3.0 ml. of acetic anhydride. The mixture was boiled for 30 min., cooled, and poured over ice. The resulting solid was recrystallized from hot ethanol water, and gave rise to 1.1 g. (0.0019 mole, 55%) of white needles melting at 231–232°. The substance was insoluble in 5% aqueous sodium hydroxide.

Anal. Calcd. for $C_{28}H_{24}N_2O_8S_2$: C, 57.92; H, 4.17; N, 4.83. Found: C, 57.91; H, 4.12; N, 4.14.

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